60453 - Structural characterization techniques

Información del Plan Docente

Academic Year	2016/17
Academic center	100 - Facultad de Ciencias
Degree	543 - Master's in Molecular Chemistry and Homogeneous Catalysis
ECTS	6.0
Course	1
Period	First semester
Subject Type	Compulsory
Module	---

1.Basic info

1.1.Recommendations to take this course

To take this course it is highly advisable a previous knowledge of instrumental and spectroscopic methods, as well as a correct understanding of technical and scientific texts in english language. The assistance to the classes and the daily study will help to overcome this course.

1.2.Activities and key dates for the course

The scheduled activities will be developed during the first semester, in several sessions of one/two hours per week. All information about schedules, calendars and exams is available at the website of the Science Faculty: https://ciencias.unizar.es/calendario-y-horarios , and the Master's website: http://masterqmch.unizar.es . The presentation of practical works will be done according with the calendar, which will be announced sufficiently in advance.

2.Initiation

2.1.Learning outcomes that define the subject

The knowledge of the physical grounds of all techniques introduced during the course, and the type of information provided by each one.

The interpretation of the information provided by the corresponding spectrum or diagram (chromatogram, voltammogram) generated by each technique, and their relationship with the structure of the compound.

For each technique, the knowledge and correct identification of its particular instrumentation, the most relevant parts and components (hardware) and their specific function.

The correct sample handling and preparation, how to perform basic experiments and to design new ones (in the cases where the technique and the software allows to do it) and how to manage the most relevant parameters of each experiment to get a given information.

To achieve an integrated vision of the whole set of techniques, being able to select the specific technique, or the particular combination of them, which are the most adequates for the correct resolution of structural problems.

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2.2.Introduction

The purpose of this course is to provide the student with a wide variety of structural tools, which generate informations usually complementaries but which can also be overlapped. We tackled here with the study of the nuclear magnetic resonance (NMR) spectroscopy, the mass spectrometry (MS), UV-Vis and fluorescence spectrophotometry, chromatographic techniques and electrochemistry. We propose a double challenge for this course: the knowledge of each individual technique and the ability to integrate the knowledges of the different techniques.

To achieve these goals we intend the study in-depth of each technique on itself, the study of the information provided by it and how this information is related with the structural determination. In addition, we intend to give an integrated perspective of the whole set of techniques as a global solution for the structural determination and/or the interpretation of a physical phenomenon.

3.Context and competences

3.1.Goals

The main goal of this course of *Structural Characterization Techniques* is to provide the student with a set of tools, in the form of techniques, focused to the structural characterization and the measurement of physical and chemical properties, which result mandatory for the research in chemical synthesis and catalysis. The course tackle the study of the most relevant, informative and useful spectroscopic, spectrometric and chromatographic techniques for research in inorganic, organic and organometallic chemistry, and in homogeneous and heterogeneous catalysis. The aim of this course is the study in depth of each technique, from the physical basis to the advanced applications, as well as the specific infrastructure of each one. Moreover, we aim to provide the student with a global perspective of the whole set of techniques and how to combine the information gathered on each one to obtain a single structural determination.

The scope of application of all studied techniques is really wide, because they are basic tools of structural determination and their knowledge is mandatory in all laboratories of chemical synthesis and catalysis. The use of these techniques is global, not only in the domain of the academic research, but also in other areas such as the medicine, the pharmaceutical industry, the food industry, quality control processes and so on.

3.2.Context and meaning of the subject in the degree

This course of *Structural Characterization Techniques* is a mandatory course of 6 ECTS, is developed during the first four-month period and belongs to the module *Structural Characterization* . The structural characterization is the cornerstone for the research on synthesis and catalysis. The meaning of this course is to provide the students with the tools to develop this task with maximal rigor. This goal is complemented with the characterization of physico-chemical properties, basis of plausible applications. This a very specialized course, where the knowledge of the different techniques is treated in-depth and strengthened in order to give to the students skills to be independent when designing new experiments and interpreting the results of each technique.

3.3.Competences

To be able to discriminate, among the different techniques, which is the most adequate to solve an specific problem or, alternatively, which is the combination of techniques providing the maximal information.

To design experiments on each technique optimizing the experimental parameters.

To be able to make a correct interpretation of the experimental data (spectra, chromatograms, voltammogram), finding their relationship with the structure.

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To be able to make a critical analysis of the data gathered and determine the accuracy level of the performed characterization.

Capacity to increase autonomally the knowledge on each technique.

Capacity to analyze critically and make assessments about a given structural determination performed using a given technique.

To be able to perform bibliographic searches about particular aspects of the different techniques and summarize clearly the key points of such publications.

3.4.Importance of learning outcomes

The determination of molecular structures is a basic point on research in chemical synthesis and catalysis. Moreover, the determination of the physical and chemical properties of new compounds through the use of different techniques, once the structure is known, allows to establish the structure-properties-applications relationship. Because all these facts, this course deals with a basic and critical key subject for the harmonic development of the others courses. Obviously some techniques can be more important than others depending of the type of research involved on each specific case, and even it could happens than one of them becomes mandatory. Anyway, two or more techniques will be necessary to reach a correct structural determination for most of the cases. As we will see, all techniques here presented are often used in almost all published works on chemical synthesis and catalysis, therefore their correct management (dominio) is very important.

4.Evaluation

The continuous evaluation during this course is based on the following activities, weighted as indicated:

1.- Homework: problem-solving and theoretical/practical questions of each technique (10%).

2.- Elaboration of a supervised individual or team-based practical work on a scientific paper (25%)

3.- Written test to be realized during the evaluation period, and which will deal with problem-solving and theoretico-practical questions (65%)

The final mark will be the best one of the following:

MARK 1: 0.1 x mark on homework + 0.25 x mark on supervised work + 0.65 x mark on writing test

MARK 2: mark on writing test

The number of official examination calls per registration and their use will be subjected to the statements of the *Regulation of Permanence in Master Studies and* *Regulation of the Learning Assessment* . The latest document will also regulate the general design and scoring criteria of the assessment activities, as well as the exam schedules and timetable for the post-examination review.

5.Activities and resources

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5.1.General methodological presentation

The learning process defined for this course is based mostly on master lectures, where the student is prompted to participate actively, complemented with classes of problem resolutions, thematic seminars and tutoring classes. This course has a clear practical and applied orientation. However, the theoretical basis of each technique are not neglected because they are mandatory for their correct understanding and for the proper data interpretation. The structure of the seminars will be that of practical sessions where the students has to tackle real problems and where the methodology for the correct analysis and interpretation of experimental data (spectra, for instance) is presented.

Most of the techniques presented along the course are used as self-service in our Institute. Therefore, in order to get an optimal information/time ratio, is mandatory to know the available experiments on each case, how to measure properly and how to extract the information contained on each set of experimental data. During the practical hands-on sessions the students will learn the different parts of the hardware of each technique and how it works, in order to gather as much information as possible in an autonomous way. For these reasons, and because the course has a strong practical character, the assistance to the practical classes is mandatory.

In addition to these activities, a practical work supervised by the different teachers will be performed. This supervised work will deal with the full structural determination of an unknown sample using the combined application of all knowledges acquired during the course in the different techniques. This structural determination will be coordinated, as much as possible, with the synthetic works developed in the couses of *Synthetic Strategies on Advanced Organic Chemistry* and *Molecular Design in Inorganic and Organometallic Chemistry.*

5.2.Learning activities

Interative magistral classes (3 ECTS).

Classes dealing with problem-solving and seminars (2 ECTS).

Hands-on practical classes on big machines (NMR, GC, and so on) (1 ECTS).

Supervised works of practical orientation.

Tutoring classes for reduced or groups or even individuals.

5.3.Program

The lecture topics to be covered are as follows:

Chapter 1 . Basics of the Nuclear Magnetic Resonance (NMR). Excitation: the nuclear spin, behaviour of the nuclear spin on the magnetic field, Larmor frequency, population of the different energy levels, transition energies, the macroscopic magnetization, the electromagnetic pulse, the resonance condition. Relaxation: T1 and T2 relaxation, the correlation time, the spectral density function, the Free Induction Decay (FID) and its mathematical treatment.

Problems. Examples of analysis of NMR spectra: chemical shift and coupling constants involving 1 H, 13 C, 19 F and 31 P nuclei.

Chapter 2. 1D experiments in NMR. Pulse programs and sequences, important parameters, the pulse-acquisition

sequence, 1 H and 19 F experiments, parameter sets. Optimizing the pulse-acquisition sequence: improving sensitivity. Double irradiation sequences, decoupling programs, advantages and disadvantages, experiments of 13 C and 31 P. Multipulse sequences, two- and three-channels configuration: the APT (J-modulated) sequence, polarization transfer, SPI, INEPT and DEPT sequences. Dynamic Nuclear Polarization.

Practical work: basic introduction to Bruker systems, routine for 1D experiments (lock, shim, rpar, wobb), measurement of 1 H and 19 F experiments. The decoupling channel, 31 P and 13 C, possibilities: power gated versus inverse gated (integration), APT and DEPT135 experiments.

Chapter 3 . The NOE effect. Origin of the NOE effect, relationship with relaxation and correlation time, steady-state NOE and transient NOE, mixing time, NOE of more than two nuclei, spin diffusion, the kinetics of the NOE, intramolecular distances, the ROE effect, the spin-lock sequence, the heteronuclear NOE.

Chapter 4 . 2D experiments. Why is necessary to perform 2D experiments?, generation of the second dimension, the evolution time. Homonuclear correlation through coupling constant (COSY, COSY-DQF and TOCSY) or through NOE effect (NOESY, ROESY). Use of pulsed-field gradients, advantages, limitations. Heteronuclear correlation through coupling constant (HETCOR, HMQC, HSQC and HMBC) or through NOE effect (HOESY). Diffusion experiments (DOSY). Selective soft pulses: 1D-NOESY.

Problems. Structural determination using chemical shif, coupling constants and NOE effects obtained from 1D and 2D experiments.

Chapter 5. Instrumental aspects. The magnet, parts; the coils, how are they built, alloys, what is a quench, field stability and homogeneity, lock and shim systems, cryoshims, shims profiles. The probe, tuning and matching, direct and inverse probes, cryoprobes, nanoprobes. The console, parts, signal generation, routing, amplification, reception, sampling, digitizers, ADC systems, gradients (concept, shape, applications), handling the FID.

Practical work: 2D experiments COSY, NOESY, HSQC, HMBC, optimization

Chapter 6. The NMR time scale, NMR dynamics, fluxional molecules, exchange. Determination of reaction rate constants: spin saturation transfer, simulation of dynamic spectra, reaction kinetics.

Problems. Kinetic and dynamic of chemical processes from the NMR

Practical work: pseudo 2D experiments, T1 measurement using the inversion-recovery method, determination of reaction rate constants

Chapter 7. Mass Spectrometry and hyphenated techniques I. Mass Spectrometry Fundamentals. Ionization systems: EI, CI, ESI, APCI, APPI, MALDI. Analyzers: Magnetic analyzer, Quadrupole mass filter, ion trap, Time of fly analyzer. Understanding mass spectra: Accurate mass measurements, isotopic pattern.

Practical work: obtaining mass spectra: ESI/APCI, MALDI. High and low resolution spectra.

Chapter 8. Mass Spectrometry and hyphenated techniques II. Tandem mass spectrometry. Metastable ions and Collision Induced dissociation. Instruments: triple quadrupole analyzer. Ion trap, hybrid spectrometers etc. Aplications of tandem mass spectrometry.

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Chapter 9 . Mass Spectrometry and hyphenated techniques III. Chromatographic methods coupled to mass spectrometry. Instrumentation: GC/MS, HPLC/MS, TLC/MS. Mixture analysis. Specialized analysis methods: Single ion Recording (SIR), Multiple Reaction Monitoring (MRM).

Practical work : GC/MS. HPLC/MS and Tandem mass spectrometry. Analysis of a complex mixture by using HPLC/MS. Fragmentation study of an organic compound in an ion Trap mass spectrometer.

Problems : Interpretation of mass spectra: accurate mass measurements, Isotopic patterns, Tandem mass spectrometry.

Chapter 10 . Ultraviolet-visible spectroscopy I. General considerations: i) Introduction and principles. ii) UV-Vis spectrophotometers. iii) Solid state studies: diffuse reflectance spectroscopy. Integrating spheres. Kubelka-Munk equation. iv) Chromophore and auxochrome groups. Isosbestic point. v) Different roles of the metal in the absorption of coordination complexes. Special behavior of lanthanides.

Problems: Protocol for UV-Vis spectra measurement. Examples of assignation of absorption bands to different transition types.

Practical work **:** Measurement of absorption and diffuse-reflectance spectra: software and sample preparation.

Chapter 11 . UV-Vis spectroscopy II. Applications: i) Colorants: Azo-derivatives, phtalocianines, formazan-derivatives. ii) Vapochromism: structural origins of vapochromism. Tools used for the analysis and description of vapochromism. Suitability of vapochromic complexes for sensoring.

Problems: UV-Vis review questions.

Chapter 12 . Luminescence I. General considerations. i) Definition and luminescence forms. ii) Light emission origin. iii) Emission and excitation spectra. iv) Spectrofluorometer. v) Lifetime and half-life of a radiative transition. vi) Quantum yield of fluorescence and phosphorescence. vii) Quenching. viii) Fluorophores. ix) Analysis of luminescent compounds.

Problems: Protocols for the measurement of: emission and excitation spectra, lifetimes and quantum yields. Assignation of the transitions responsible for the luminescence in different compounds.

Practical work: Emission and excitation spectra measurements: software and sample preparation.

Chapter 13 . Luminescence II: Applications. i) Phosphorescent compounds for OLEDs: principles and set-up of an OLED. The role and characteristics of phosphorescent compounds for OLEDs. ii) Fluorescence sensing.

Problems: Luminescence review questions

Chapter 14. Electrochemical techniques I. Basic concepts: electron-transfer and energy levels, concentrations and potential (Nerst's equation), kinetics of the electron-transfer reactions (Butler-Volmer's equation), mass transport (Fick's laws).

Chapter 15. Electrochemical techniques II. Potential step voltammetry (Cottrell's equation), lineal voltammetry (Randles-Sevick's equation), cyclic Voltammetry (chemical reversibility).

Practical work: Basic introduction to potentiostat/galvanostat E&G, sample preparation, CV waves (Vi, Vf, Vs, scan rate).

5.4.Planning and scheduling

The timetable of this course and the dates of the exams will be published in the bulletin board and in the webpage of the Sciences Faculty . The exposition of practical works will be done according with the calendar, which will be announced well in advance.

The students will be provided with diverse teaching material either at reprography or through the University's web tool: https://moodle2.unizar.es/add .

5.5.Bibliography and recomended resources

Basic Bibliography

- Determinación structural de compuestos orgánicos. E. Pretsch, P. Bühlman, C. Affolter, A. Herrera, R. Martínez. Springer, NY, 2000.
- Applied NMR Spectroscopy for Chemists and Life Scientists, first edition. Oliver Zerbe and Simon Jurt. Ed. Wiley-VCH, Weinheim, Germany 2014.
- Mass Spectrometry Basics. C. G. Herbert, R.A.W. Johnstone. CRC Press 2003.
- Optical spectroscopy in chemistry and life sciences. An introduction. W. Schmidt, Ed. WILEY-VCH 2005.
- Electrochemical Methods: fundamentals and applications 2nd ed, A. J. Bard, L. R. Faulkner, John Wiley&Sons, INC, New York 2001.

Complementary Bibliography

In general, the complementary bibliography will be based on research articles published on international journals, which will be updated every year. In addition, we suggest the following textbooks:

- Espectroscopia. A. Requena, J. Zúñiga. Pearson/Prentice Hall, 2005.
- Basic One- and Two-dimensional NMR Spectroscopy, fifth revised edition. H. Friebolin. Ed. Wiley-VCH, Weinheim, Germany 2010.
- NMR in Organometallic Chemistry, first edition. Paul S. Pregosin. Ed. Wiley-VCH, Weinheim, Germany 2012.
- High Resolution NMR Techniques in Organic Chemistry, second edition. T. D. W. Claridge. Tetrahedron Organic Chemistry Series, volume 27. Ed. Elsevier, 2009.
- 200 and More NMR Experiments. S. Berger and S. Braun. Ed. Wiley-VCH, Weinheim, Germany 2004.
- Understanding NMR Spectroscopy. J. Keeler. Ed. Wiley-VCH, Weinheim, Germany 2006.
- Liquid Chromatography-Mass Spectrometry. Third Edition. W. M.A. Niessen. CRC 2006.
- Mass Spectrometry/Mass Spectrometry, Techniques and Applications of Tandem Mass Spectrometry. K.L.Busch, G.L.Glish, S.A.McLuckey. Wiley VCH 1988.
- Liquid Chromatography-Mass Spectrometry: An Introduction. R. E. Ardrey. Willey-VCH 2003.
- Gas Chromatography and Mass Spectrometry. A Practical Guide. F. G. Kitson, B. S. Larsen, C. N. McEwen. Academic Press 1996.
- Principles of Fluorescence Spectroscopy. J. R. Lakowicz. Springer 2006.
- Laboratory Techniques in Electroanalytical Chemistry 2nd ed, P. T. Kissinger, W. R. Heineman Eds., Marcel Dekker, Inc, New York 1996.